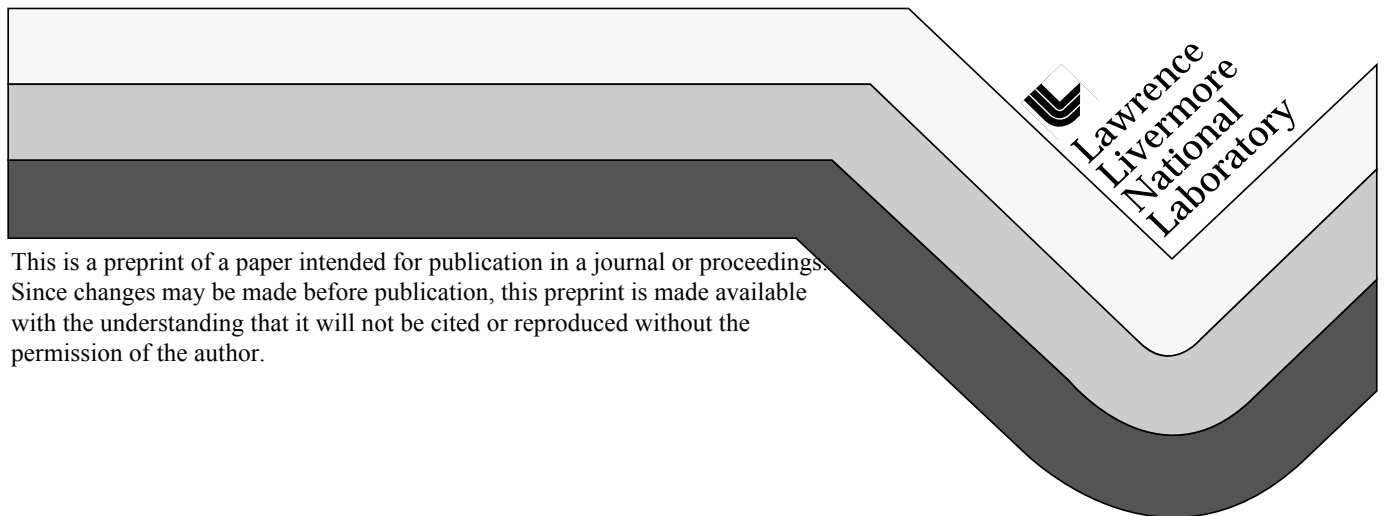


Immobilization of Uranium and Plutonium into Borobasalt, Pyroxene and Andradite Mineral-like Compositions

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Abstract

The immobilization of plutonium-containing wastes into stable solid compositions is one of the problems to be solved in the disposal of radioactive wastes. Research efforts on the selection, preparation with the use of the cold crucible induction melter (CCIM) technology, and investigation of materials that are most suitable for immobilizing plutonium-containing wastes of different origin have been carried out at the All-Russian Scientific Research Institute of Inorganic Materials (VNIINM) and the Institute of the Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry (IGEM), Russian Academy of Sciences within the framework of agreements with Lawrence Livermore National Laboratory (LLNL, USA) regarding material and technical support.

This paper presents the data on the synthesis of cerium-, uranium-, and plutonium-containing materials based on borobasalt, pyroxene, and andradite compositions in the muffle furnace and by the CCIM method. Compositions containing up to 15-18 wt% cerium oxide, 8-11 wt% uranium oxide, and 4.6-5.7 wt% plutonium oxide were obtained in laboratory facilities installed in glove boxes. Comparison studies of the materials synthesized in the muffle furnace and CCIM demonstrate the advantages of using the CCIM method. The distribution of components in the materials synthesized were investigated, and certain of their physicochemical properties determined.

Introduction

The progress of nuclear power engineering and nuclear technology as a whole is associated with solving the problems of the nuclear fuel cycle, including the disposal of long-lived radioactive wastes that require long-term and safe storage.

The necessity of isolating radioactive wastes from the environment over a long period of time and the desire to shorten the repository service period require immobilization of radionuclides and other biologically hazardous waste components into solid forms. Solidified compositions should possess the necessary thermal durability, radiation resistance, high chemical resistance, and mechanical stability and also provide sufficient stability during storage and burial.

At present, the immobilization of wastes in the form of vitreous, mineral-like, glass-ceramic, and ceramic compositions is considered to be the most promising method for their long-term storage and subsequent burial.

Research efforts on the selection, preparation with cold crucible induction melter (CCIM) technology, and investigation of materials that are most suitable for immobilizing plutonium-containing wastes of different origin have been carried out at the All-Russian Scientific Research Institute of Inorganic Materials (VNIINM) and the Institute of the Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry (IGEM), Russian Academy of Sciences within the framework of the agreements with Lawrence Livermore National Laboratory (LLNL, USA) on material and technical support.

The paper presents data on the synthesis of cerium-, uranium-, and plutonium-containing materials based on borobasalt (Bz), pyroxene (JED), and andradite (A) compositions in a muffle furnace and a CCIM.

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Experimental

Based on analysis of compositions of the possible plutonium-containing wastes, the borobasalt vitreous matrices and also pyroxene and ferrosilicate (andradite) compositions were chosen as matrix materials for the immobilization.

Preparation of Vitreous and Mineral-Like Compositions

Cerium-, uranium-, and plutonium-containing vitreous borobasalt compositions (Table 1) were prepared in laboratory facilities, i.e., alundum crucibles in muffle furnaces (Fig. 1a) and CCIM (Fig. 1b) installed in glove boxes.

Table 1. Calculated compositions of synthesized materials.^a

Oxide	Oxide content, wt%						
	Muffle furnace			CCIM			
	Bz-Ce-15	Bz-U-10	Bz-Pu-5	Bz-Na	Bz-Na-Ce-15	Bz-Na-U-10	Bz-Na-Pu-5
Na ₂ O	1.7	1.8	1.9	6.0	5.0	5.5	5.7
MgO	4.3	4.6	4.9	3.0	2.5	2.8	2.9
Al ₂ O ₃	7.2	7.6	8.1	10.0	8.3	9.2	9.6
SiO ₂	25.9	27.4	28.9	35.0	29.2	32.2	33.7
K ₂ O	0.3	0.3	0.3	1.0	0.8	0.9	0.9
CaO	14.9	15.8	16.6	15.0	12.5	13.8	14.4
TiO ₂	0.5	0.5	0.5	1.0	0.8	0.9	0.9
MnO	0.1	0.1	0.1	0	0	0	0
Fe ₂ O ₃	5.2	5.5	5.8	6.0	5.0	5.5	5.7
B ₂ O ₃	24.9	26.4	27.9	23.0	19.2	21.2	22.2
CeO ₂	15.0	0	0	0	16.7	0	0
U ₃ O ₈	0	10.0	0	0	0	8.0	0
PuO ₂	0	0	5.0	0	0	0	4.0

^aCalculations were carried out for the preparation of 150 g of melted material block.

The materials were synthesized by melting mixtures of a preliminarily prepared borobasalt glass frit with the desired oxides (CeO₂, U₃O₈, or PuO₂) incorporated into the composition at a temperature of 1200-1300°C for 1-3 hours.

Cerium-, uranium-, and plutonium-containing compositions of the pyroxene and andradite types (Table 2) were prepared in the laboratory CCIM facilities (Fig. 1b). The materials were synthesized by melting of mixtures of a previously prepared matrix frit with the desired oxides (CeO₂, U₃O₈, or PuO₂) incorporated into the composition or oxide-salt mixtures at a temperature of 1500-1600°C for 0.5-1 hour.



a



b

Fig. 1. Glove boxes with (a) muffle furnace and (b) CCIM.

Table 2. Compositions of materials synthesized in CCIM.^a

Oxide	Oxide content, wt%															
	JED-F		JED-Ce		JED-U		JED-Pu		A-F		A-Ce		A-U		A-Pu	
	calcd	as-an	calcd	as-an	calcd	as-an	calcd	as-an	calcd	as-an	calcd	as-an	calcd	as-an	calcd	as-an
SiO ₂	42.0	55.0	35.8	42.6	38.1	42.9	40.1	n/a	38.0	50.6	32.3	37.5	34.0	43.0	35.9	n/a
MgO	16.0	9.0	13.6	8.2	14.5	14.5	15.3	n/a	8.0	6.8	6.8	6.1	7.1	6.7	7.6	n/a
Al ₂ O ₃	8.0	9.5	6.8	8.2	7.3	9.0	7.6	n/a	12.0	14.6	10.2	13.6	10.7	12.5	11.3	n/a
CaO	14.0	11.0	11.9	9.7	12.7	9.5	13.4	n/a	11.0	8.1	9.4	7.2	9.8	10.0	10.4	n/a
Fe ₂ O ₃	12.0	8.0	10.2	9.8	10.9	9.5	11.4	n/a	26.0	15.9	22.1	14.3	23.2	14.5	24.6	n/a
NiO	-	-	-	-	-	-	-	-	1.0	0.4	0.9	0.5	0.9	0.2	0.9	n/a
Cr ₂ O ₃	-	-	-	-	-	-	-	-	2.0	1.8	1.7	1.4	1.8	0.1	1.9	n/a
MnO ₂	-	-	-	-	-	-	-	-	2.0	1.8	1.7	1.6	1.8	1.8	1.9	n/a
Na ₂ O	8.0	7.5	6.8	6.1	7.3	5.8	7.6	n/a	-	-	-	-	-	-	-	-
CeO ₂	-	-	14.9	15.4	-	-	-	-	-	-	14.9	17.8	-	-	-	-
U ₃ O ₈	-	-	-	-	9.2	8.6	-	-	-	-	-	-	10.7	11.2	-	-
PuO ₂	-	-	-	-	-	-	4.6	4.6	-	-	-	-	-	-	5.5	5.7

^aJED block - 130 g, A block - 110g, n/a – not analyzed.

Investigation of Prepared Materials

Borobasalt Compositions

The borobasalt compositions (Bz-U-10 and Bz-Pu-5) synthesized in the muffle furnace are the vitreous materials, whose bulk glass contains dispersed crystalline particles consisting of uranium and plutonium oxides that are undissolved or crystallized from a melt (Fig. 2). The solubility of uranium and plutonium in the compositions synthesized in the muffle furnace is limited to 9.6 and 3.5 wt%, respectively. Excess uranium precipitates out as a sediment to form a thin layer of crystalline phase in the bottom part of the glass block (Figs. 2a, 2b). The layer is predominantly composed of two types of tiny crystals 1-5 (rarely 10) microns in size with glass-filled gaps in between. The crystals of the first predominant type (Fig. 2b, n1) form aggregates comprising tiny rounded grains that are closely adjacent to each other. The crystals of the second type (Fig. 2b, n2) form 4-ray and 6-ray aggregates that are several microns in size. These crystals are close in composition to the crystals of the first type. Uranium is the predominant component, and calcium is observed in smaller amounts (6-8 wt%) (Table 3).

Excess plutonium predominantly precipitates out as a sediment to form a layer of crystalline phase in the bottom part of the glass block (Figs. 2c, 2d). Single crystalline particles and their aggregates occur in the bulk of the glass block, which was held in the molten state for 3 hours. The borobasalt compositions (Bz-Na-U-10 and Bz-Na-Pu-5) synthesized in the CCIM are homogeneous glasses with a uniform distribution of uranium and plutonium at an average content of 8.2 and 5.6 wt%, respectively (Fig. 3).

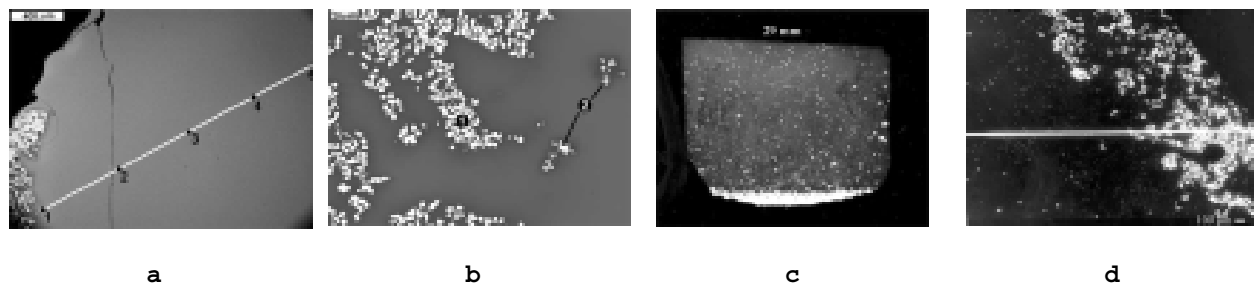


Fig. 2. (a, b, d) SEM and (c) radiographic images of (a, b) Bz-U-10 and (c, d) Bz-Pu-5 samples.

Table 3. As-analyzed compositions of uranium-containing crystalline phases in the glass Bz-U-10.

Crystal type	Oxide content, wt%				
	Al ₂ O ₃	SiO ₂	CaO	Fe ₂ O ₃	UO ₂
1	1.7	1.5	7.1	0.7	80.8
1	2.1	3.5	8.35	0.5	78.1
2	0.6	0.6	6.6	-	1.1
2	0.6	0.7	6.3	-	83.7

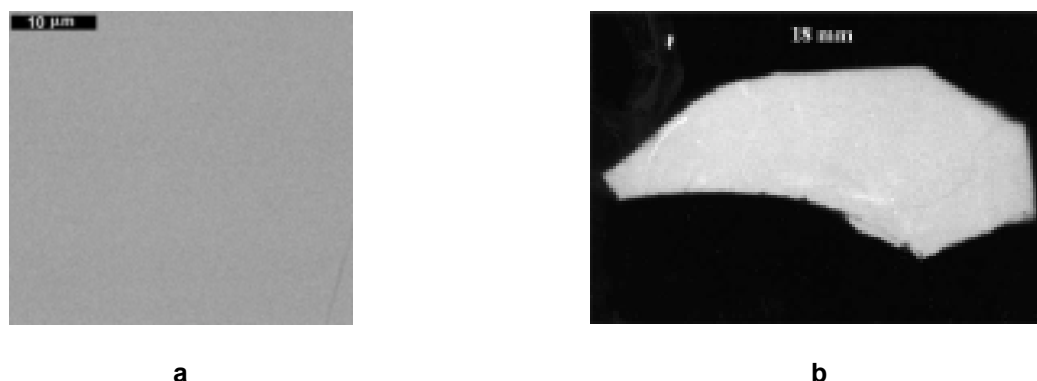


Fig. 3. (a) SEM and (b) radiographic images of (a) Bz-Na-U-10 and (b) Bz-Na-Pu-5 samples.

Pyroxene and Andradite Mineral-like Compositions

The uranium-containing JED-U block synthesized in the CCIM is composed of the glass and crystalline phases. The block exhibits a pronounced zonal structure. The first (upper) zone consists of a homogeneous glass (Fig. 4a, Table 4). The central zone (about 5 mm thick) is comprised of a glass and the crystalline aggregate (Figs. 4b-4d, Table 4). The bottom zone (bottom slag lining) has an inhomogeneous structure (Fig. 4e, Table 4). In the synthesized block, uranium is dissolved in

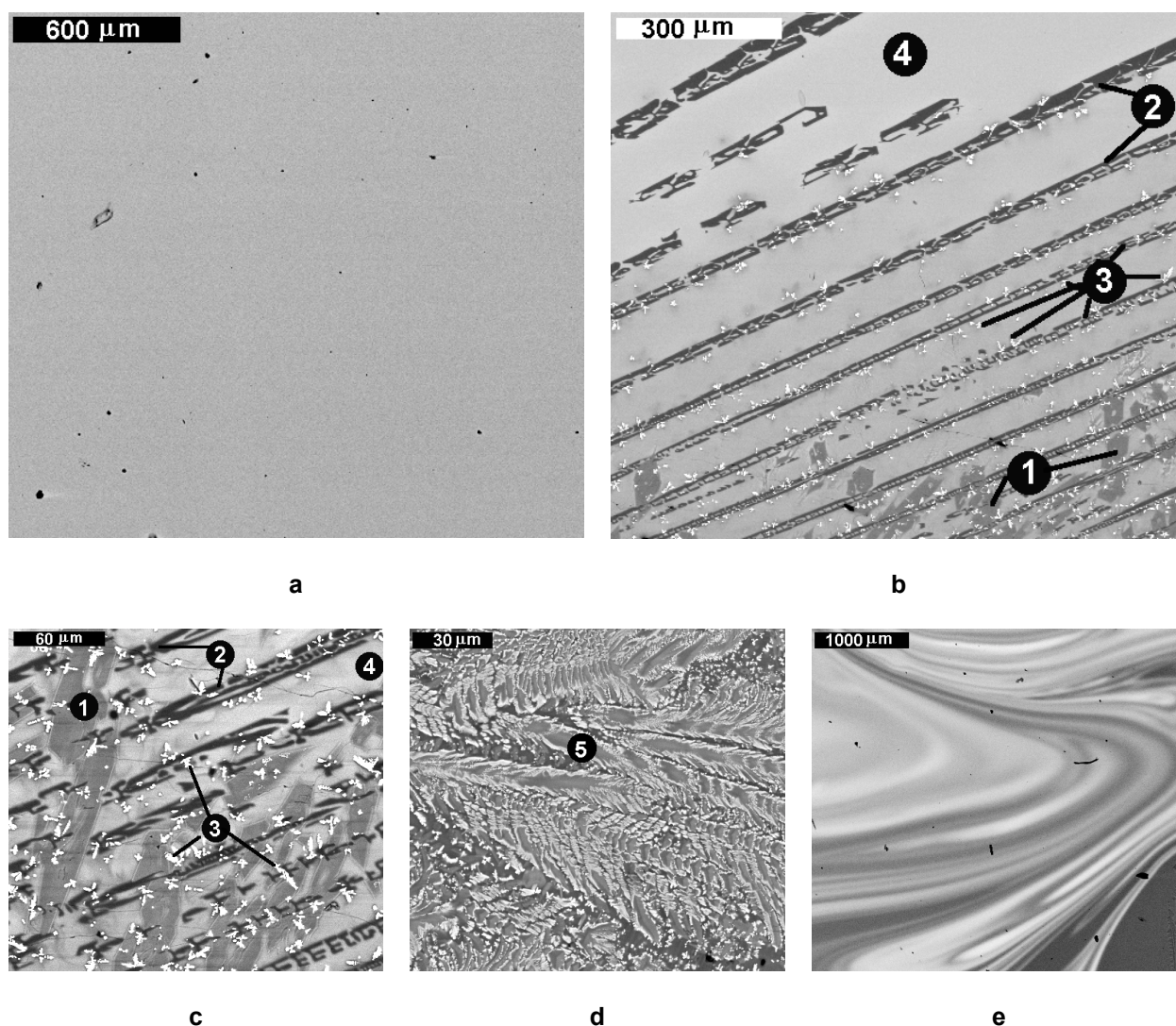


Fig. 4. SEM (reflection electrons) images of JED-U samples: (a) upper (first) zone of block, (b) upper part of the central (second) zone of block, (c) central part of the central (second) zone of block, (d) bottom part of the central (second) zone of block, and (e) bottom (third) zone of block: (1) fassaite, (2) forsterite, (3) uranium oxide, (4) glass, and (5) aggregate of fassaite and forsterite microcrystals in the uranium-rich glass.

considerable amounts in the glass phase of the first main zone of the block. In this zone the uranium content is equal to about 8.6 wt%. In the central part of the block, uranium is also observed in the form of submicroscopic star-shaped crystals identified as synthetic uranium oxide UO_2 ; these are uniformly distributed throughout the crystalline aggregate.

The uranium-containing A-U block synthesized in the CCIM consists of glass (60-80%) and crystalline spinel phases (20-40%) (Fig. 5, Table 5). Uranium occurs only in the glass phase, in which its content is equal to about 11 wt%.

The investigation of the samples of the plutonium-containing pyroxene composition JED-Pu synthesized in the CCIM demonstrated that plutonium is uniformly distributed over the glass in the upper and central zones of the block. The mass of the block is about 130 g. Its average concentration is equal to 4.6 wt% PuO_2 (Fig. 6a, Table 6).

Table 4. Glass compositions in different parts of the JED-U block (SEM/EDS).

Oxide wt%	Under crystalline aggregate								Between crystals		Over crystalline aggregate		
	1	2	3	4	5	6	7	8	1	2	1	2	3
Na ₂ O	4.2	4.1	3.9	3.6	3.4	4.3	4.0	3.9	4.4	4.7	4.1	3.9	3.9
MgO	13.5	15.4	15.1	14.4	16.5	14.1	11.6	13.3	4.3	9.6	14.2	14.8	14.6
Al ₂ O ₃	9.3	5.8	7.1	6.8	7.1	7.2	7.9	8.6	9.2	11.5	11.0	10.7	11.0
SiO ₂	48.9	47.5	47.5	47.1	44.9	44.1	46.9	46.5	43.8	44.7	46.7	45.3	45.8
CaO	11.9	11.8	12.0	12.2	12.2	10.7	11.1	11.5	14.3	13.3	11.3	11.5	11.7
Fe ₂ O ₃	8.5	8.7	8.1	8.6	8.7	8.4	8.8	8.9	9.5	9.2	8.7	8.4	8.9
UO ₂	1.7	4.3	6.1	7.8	8.6	9.6	10.3	11.5	11.7	10.4	8.8	8.4	8.5

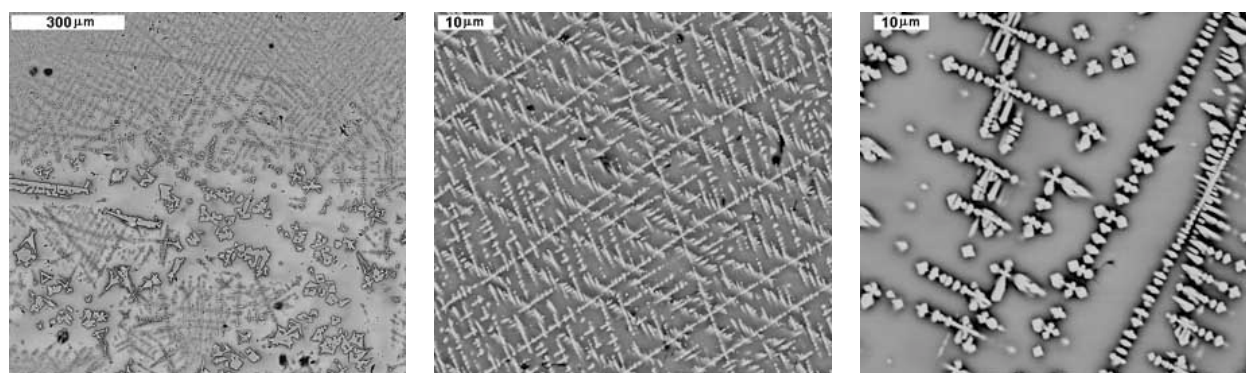


Fig. 5. SEM/EDS images of the upper (main) part of the A-U block; spinel (white) , glass (gray) .

Table 5. Glass compositions in different parts of the sample according to SEM/EDS.

Oxide wt%	Central part of block			Main part of block				
	Glass			Glass	Glass + crystal (15x15 μm)			
	1	2	average	1	1	2	3	average
Fe ₂ O ₃	14.6	14.2	14.4	10.2	18.7	19.4	19.5	19.3
CaO	9.9	10.1	10.0	10.4	8.6	7.02	8.7	8.2
SiO ₂	43.0	43.3	43.1	46.9	40.5	39.9	39.1	39.6
Al ₂ O ₃	12.8	12.0	12.4	11.7	12.1	13.5	11.9	12.3
MgO	6.5	6.8	6.7	6.3	6.7	6.5	6.0	6.3
UO ₂	10.8	11.6	11.2	11.9	9.9	9.9	9.4	9.7
MnO	1.8	1.8	1.8	1.6	1.7	1.6	1.7	1.7
NiO	0.3	0.2	0.2	0.1	0.6	0.7	0.6	0.7
Cr ₂ O ₃	-	0.1	0.1	-	1.3	1.5	1.4	1.4

In the plutonium-containing garnet composition A-Pu synthesized in the CCIM, plutonium is also uniformly distributed in the upper and central zones of the block. The mass of the block is about 100 g. Its average concentration is equal to 5.7 wt% PuO₂ (Fig. 6b, Table 7).

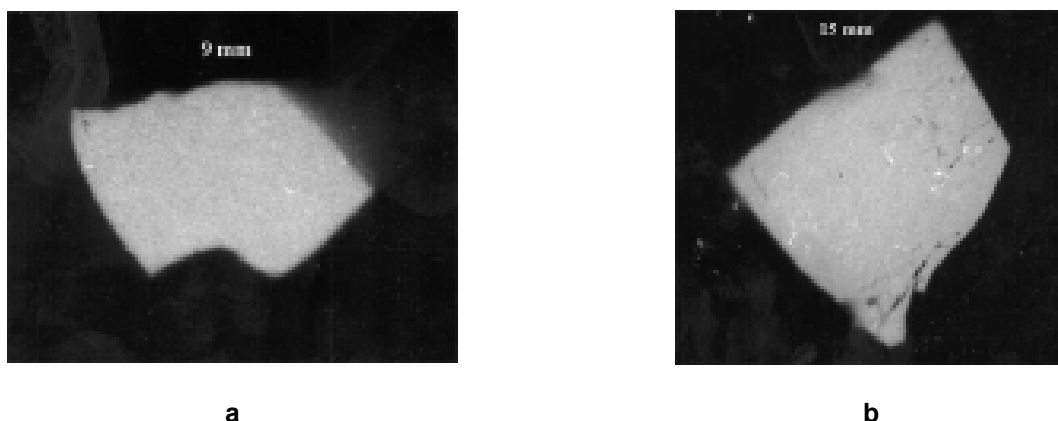


Fig. 6. Radiographic images of (a) JED-Pu and (b) A-Pu samples.

Table 6. Data of profile probing for the JED-Pu composition (probing step, 500 μm).

Point of probing													
1	2	3	4	5	6	7	8	9	10	11	12	13	14
Plutonium content, wt% PuO_2													
4.6	4.4	4.6	4.8	4.6	4.4	4.3	4.6	4.5	4.5	4.7	4.8	4.2	4.6

Table 7. As-analyzed plutonium contents in samples of the A-Pu composition (gamma spectrometry).

Sample													
1	2	3	4	5	6	7	8	9	10	11	12	13	14
Plutonium content, wt% PuO_2													
6.4	5.5	5.1	6.1	5.8	5.5	5.3	6.1	5.7	5.7	5.8	5.3	5.5	6.1

Conclusions

These investigations showed that the use of the CCIM method for the immobilization of radioactive wastes makes it possible to produce homogeneous glasses, which are characterized by a uniform distribution of uranium and plutonium at concentrations of 10 and 5 wt%, respectively. It should be noted that the crystalline phases (pyroxene and garnet) were not obtained in any case. It is clear that this is associated with the ability of silicate melts to form the vitreous state upon their rapid cooling (quenching).

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